

**PCT**

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C07C 17/395, 19/08</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/37955</b> <b>(43) International Publication Date:</b> 16 October 1997 (16.10.97)
<b>(21) International Application Number:</b> PCT/US97/05656 <b>(22) International Filing Date:</b> 4 April 1997 (04.04.97)  <b>(30) Priority Data:</b> 08/628,064      4 April 1996 (04.04.96)      US  <b>(71) Applicant:</b> ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). <b>(72) Inventors:</b> YATES, Stephen, Frederic; 1539 S. Kennicott Drive, Arlington Heights, IL 60005 (US). GAITA, Romulus; 6646 Davis Street, Morton Grove, IL 60053 (US). <b>(74) Agent:</b> CRISS, Roger, H.; AlliedSignal Inc., Law Dept. (C.A. McNally), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).		<b>(81) Designated States:</b> JP, KR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PURIFICATION OF 1,1,1,3,3-PENTAFLUOROPROPANE (R-245fa)  <b>(57) Abstract</b>  1-Chloro-3,3,3-trifluoropropene (R-1233zd) or other olefin impurities are removed from 1,1,1,3,3-pentafluoropropane (R-245fa) by contacting the R-245fa in the liquid or vapor phase with chlorine in the presence of ultraviolet light providing an exposure of at least about 0.02 watts-hour/kg.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LJ	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

PURIFICATION OF 1,1,1,3,3-PENTAFLUOROPROPANE (R-245fa)

BACKGROUND OF THE INVENTION

This invention relates principally to the purification of 1,1,1,3,3-  
5 pentafluoropropane, also designated R-245fa, which has been of particular interest as a  
replacement for chlorofluorocarbons having similar physical properties, particularly  
R-113. R-245fa may be prepared by a three-step process involving reaction of  
chloroform,  $\text{CCl}_4$ , with vinylidene chloride,  $\text{CH}_2=\text{CCl}_2$ , reacting the product with HF  
to form  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  (R-235fa) and finally, hydrogenation to remove the chlorine  
10 atom, as disclosed in pending U.S. Serial No. 08/099,676.

It is characteristic of such reactions that many by-products are formed,  
containing varying numbers of hydrogen, chlorine, and fluorine atoms on  $\text{C}_1\text{-C}_3$   
compounds. These by-products and the unreacted feed material may be separated by  
distillation where possible. Some compounds are relatively harmless since their  
15 presence does not greatly alter the physical properties for which R-245fa is useful.  
One by-product which must be removed because of its toxicity is 1-chloro-3,3,3-  
trifluoropropene (R-1233zd), although only relatively small amounts are typically  
present in R-245fa as formed. R-1233zd has a boiling point close to that of R-245fa  
making them difficult to separate by distillation. After distillation of the crude  
20 product, R-1233zd will still be present in amounts from about 300 to 20,000 ppm  
(wt.). It should be reduced to below 20 ppm according to the specifications of the  
Panel for Advancement of Fluorocarbon Test (PAFTII). Preferably, the R-1233zd  
should be below about 10 wt. ppm.

Further improvement in methods of purifying R-245fa, particularly with  
25 respect to eliminating R-1233zd is desired and the present inventors have discovered a  
means for purification by photochlorination which will be disclosed in detail below.

In addition to R-1233zd, there may be several other unsaturated by-  
products present which would be expected to be removed by a process which removes  
R-1233zd, for example, R-1223xd, R-1224zb, R-1224xe, R-1233xf, and the like

### SUMMARY OF THE INVENTION

1-chloro-3,3,3-trifluoropropene (R-1233zd) is removed from a mixture consisting substantially of 1,1,1,3,3-pentafluoropropane (R-245fa) and containing up to about 20,000 wt. ppm R-1233zd by contacting the R-245fa mixture with 1-5 mols of chlorine for each mol of R-1233zd in the presence of ultraviolet light having a wave  
5 length between about 300 to 400 nm which provides at least 0.02 watts-hour/kg of the mixture, preferably 0.02 to 2.0 watts-hour/kg. The R-1233zd can be reduced to below 10 wt. ppm or lower, as it is converted to 1,2,2-trichloro-3,3,3-trifluoropropane (R-233) or other propanes containing more chlorine such as R-223 or R-213, which have  
10 higher boiling points and can be easily separated from R-245fa. Other unsaturated compounds, such as R-1233xd, R-1224zb, R-1224xe, and R-1233xf, are also removed by chlorination to other derivatives which can be separated, for example by distillation. The temperature and pressure used may be adjusted to provide R-245fa in either the vapor or liquid phase, the liquid phase being preferred.

15 The photochlorination of R-245fa may produce as a by-product 3-chloro-1,1,1,3,3-pentafluoropropane (R-235fa).

### DETAILED DESCRIPTION OF THE INVENTION

R-245fa may be produced by the process of USSN 08/099,676, beginning from chloroform and vinylidene chloride. The crude product will contain a  
20 variety of byproducts. It is of particular importance to remove 1-chloro-3,3,3-trifluoropropene (R-1233zd) from the crude product. Preliminary separation of R-245fa by distillation will leave about 300 to 20,000 wt. ppm of R-1233zd having a boiling point of 19.2°C compared to 15.3°C for R-245fa, the difference in boiling  
25 points making R-1233zd difficult to separate from R-245fa. In the process of the invention, R-1233zd or other unsaturated compounds which may be present, e.g. R-1233xd, R-1224zb, R-1224xe, R-1233xf, are reacted with chlorine to provide more highly chlorinated compounds which have a higher boiling point and can be readily

separated from R-245fa. Optionally, R-235fa may be co-produced by chlorination of R-245fa.

#### Process Conditions

5                   In the process, crude R-245fa containing about 300 to 20,000 wt. ppm of R-1233zd along with minor amounts of other byproducts such as those mentioned above will be contacted with chlorine in the presence of ultraviolet light having a wavelength of about 300 to 400 nm. It should be understood that an ultraviolet lamp may have radiation outside this range also, but that photochlorination requires UV  
10                   light within this range.

                  The ultraviolet light will have an intensity which provides an exposure greater than zero and at least about 0.02 watts-hour/kg of the R-245fa mixture, preferably 0.02 to 2.0 watts-hour/kg.

                  The ultraviolet light may be provided by arc lamps including mercury,  
15                   argon, or xenon and filament lamps including tungsten and halogen.

                  Chlorine is introduced into the crude R-245fa stream at a rate sufficient to provide about 1 to 5 mols of chlorine for each mol of R-1233zd, preferably 1 to 1.5.

                  It has been found that increasing either the ratio of chlorine to R-1233zd ( $\text{Cl}_2/\text{R-1233zd}$ ) or the ultraviolet light exposure improves the chlorination of  
20                   R-1233zd. Generally, we have been able to reduce the R-1233zd to below 10 wt. ppm using a UV exposure above about 0.04 watts-hour/kg but with quite low ratios of  $\text{Cl}_2/\text{R-1233zd}$ . Conversely, much lower UV exposures can be used if higher  $\text{Cl}_2/\text{R-1233zd}$  ratios are used. The  $\text{Cl}_2/\text{R-1233zd}$  ratio and UV exposure may be adjusted to provide the desired set of conditions.

25                   The temperature employed may vary but may be from about  $-50^\circ\text{C}$  to  $200^\circ\text{C}$ , preferably about  $25^\circ$  to  $60^\circ\text{C}$ .

                  The pressure selected will be a convenient value to suit the processing conditions for R-245fa and to assure that R-245fa is a liquid or vapor, as desired.

The UV radiation from a lamp ordinarily will be expressed as watts, which is a rate of delivering energy. For present purposes, it is considered more useful to express radiation as the quantity of energy delivered over a period of time, i.e. the "exposure," rather than as the rate. Thus, the exposure may be expressed as watts-hours, which is related to the number of photons of energy delivered and their wavelength and these, in turn, relate to the chlorination of unsaturated molecules such as R-1233zd. Since the exposure is the product of the rate of delivering energy (photons/time) and the time, it will be clear that either the rate or the time could be varied. However, for practical applications the rate and the time will have limits imposed by the need to carry out the desired photochlorination reaction within constraints of time and product yield. If a high rate or a long time is used, not only will R-1233zd be chlorinated to R-233 (or R-223 or R-213), but chlorine will react with other molecules, particularly with R-245fa to make R-235fa. Alternatively, if a very low rate or a short time is used, then insufficient chlorination of R-1233zd would be expected.

When co-production of 3-chloro-1,1,1,3,3-pentafluoropropane (R-235fa) is desired, the ratio of chlorine to R-245fa can be increased. Preferably, the U.V. exposure will be about 1.5 to 5.0 watts-hour/kg of R-245fa and the  $\text{Cl}_2/\text{R-1233zd}$  ratio (mol) about 1-50 to 1. It will be understood by those skilled in the art that the operating conditions may be adjusted to optimize the relative amounts of R-235fa and R-245fa.

After the R-245fa has been photochlorinated, the chlorinated products may be separated from the R-245fa, as, for example, by distillation, since the boiling points are no longer close to that of R-245fa. Any residual chlorine, HCl or HF may be separated by absorption of chlorine in aqueous caustic, by adsorption on carbon molecular sieves, or reaction with aqueous sodium sulfite or sodium thiosulfate.

Example 1Liquid phase purification of R-245fa

The photochlorination of R-245fa was carried out in a 125 mL pyrex pressure vessel equipped with a dip leg inlet and a pressure gauge. This vessel was chilled in ice water and 20.0 grams of impure G-245fa, containing 0.08% R-1233zd was condensed into it. Then, while still cold, a stream of chlorine gas was passed at 10 mL/min through this solution for exactly 52 seconds. We calculate according to the ideal gas law that this should correspond to  $3.6 \times 10^{-4}$  moles of chlorine, or a 1:1 mole ratio with the R-1233zd impurity. The vessel was then allowed to warm to room temperature.

The reactor vessel was placed for 5 minutes at the focus of RPR-100 Rayonet reactor (Southern New England Ultraviolet Company) equipped with 16 RPR-3500 lamps having their peak intensity at a wavelength of 350 nm. Light below 300 nm was removed by the pyrex walls of the pressure vessel. Ferrioxalate actinometry was used to measure the radiation received (see The Chemists Companion, A. J. Gordon & R. A. Ford, Wiley Interscience (1972), pages 362-368). In this vessel under these conditions this procedure gave an incident light intensity of  $1.317 \times 10^{-7}$  einstein/sec (0.0417 watts). (One einstein is an equal to a mol of photons.) A five minute exposure should therefore have supplied  $3.95 \times 10^{-5}$  einsteins of light (0.039 watt-hour/kg).

After exposure, the vapor head of the pressure vessel was sampled by gas chromatography using a 3048 mm long x 3.175 mm diameter column of 1% SP1000 on 60-80 mesh Carbopack B (Supelco Inc.) packing operated at 45°C for 3 minutes and then programmed to increase 8°C/min to 200°C. This stream contained 0.00335 % R-1233zd, and 0.0793 % R-235fa.

Example 2Vapor phase purification of R-245fa

The photochlorination of R-245fa was carried out in a 125-mL pyrex pressure vessel equipped with an inlet at the bottom and an outlet at the top. The reactor vessel was placed at the focus of RPR-100 Rayonet reactor (Southern New

England Ultraviolet Company) equipped with 16 RPR-3500 lamps having their peak intensity at a wavelength of 350 nm. Light below 300 nm was removed by the pyrex walls of the vessel. The vessel was immersed in a pyrex constant temperature bath held at 59 °C to ensure that the G-245fa remained in the vapor phase.

Two feed streams were passed through separate lengths of capillary tubing and then mixed and passed into the reactor at 5 psig (34.5 kPa gauge). The impure R-245fa contained 0.080 % R-1233zd plus other impurities. One stream contained impure R-245fa while the second contained chlorine. By blending the two streams the ratio of chlorine to R-1233zd was varied. The radiation exposure was calculated from the residence time and the light intensity and varied from 2 to 3.5 watts-hour/kg. After exposure to the ultraviolet light the product stream was analyzed by gas chromatography using the procedures of Example 1.

The results of the tests at lower ratios of  $\text{Cl}_2/\text{R-1233zd}$  are given in Table 1. The compounds are designated as refrigerants (R) according to the commonly used system of the American Society of Refrigerating Engineers.

Table 1  
Vapor Phase Photochlorination to Remove Olefinic Impurities

R-245fa Flow Rate (mL/min)	Chlorine Flow Rate (mL/min)	Estimated Chlorine/G-1233zd Molar Ratio	Conc. R-1233zd (%)	Conc. R-235fa (%)
Feed	—	—	0.0800	0.00091
49	3.0	26.5	0.0080*	1.232
49	5.7	48.0	N.D.	8.789
91	0.99	4.7	0.00319	2.554

\* value suspect, R-1233zd concentration should have been low since R-235fa has been produced.



Example 3Effect of Chlorine Ratio on R-245fa Purity

A series of experiments were done using the same general procedure as that described in Example 1. However, for each experiment, the weight of G-245fa, and the amount of chlorine introduced was changed, so as to explore the effect of changing the ratio of these reactants. All samples were exposed to UV light as described in Example 1 for 1 minute. Then GC analysis was completed as described. The amounts of reagents and experimental results are shown in Table 2 below.

Table 2Effect of Chlorine Ratio on Performance in Liquid Phase

Weight G-245fa (g)	Chlorine Flow rate (mL/min)	Chlorine Flow time (sec)	Calculated Moles Chlorine ( $\times 10^5$ )	Calculated $\text{Cl}_2/\text{R-1233zd}$ Molar Ratio	Conc. of R-1233zd (%)	Conc. of R-235fa (%)
Feed	—	—	—	—	1.04	0.0027
17.3	2.97	30	5.8	0.096	0.935	N.D.
21.5	10.33	30	20.3	0.27	0.54	0.01
9.5	10.32	24	16.2	0.495	0.40	0.191
8.20	10.34	32	21.6	0.76	0.017	1.85
11.8	10.34	60	40.6	1.00*	0.829*	N.D.*
23.7	10.33	160	108.1	1.22	0.0003	0.66
23.9	10.33	180	121.6	1.47	N.D.	4.05

\*Air contamination suspected, which will prevent the photochlorination from occurring.

It can be seen that the concentration of R-1233zd decreases as the ratio of  $\text{Cl}_2/\text{R-1233zd}$  is increased. Theoretically one mol of chlorine can react with one mol of R-1233zd to yield one mol of R-233. The results show that at a ratio of about

1.47/1 essentially all of the R-1233zd has been converted within the limits of analytical precision. The product of chlorination of R-245fa, i.e., R-235fa is seen to appear at a ratio of about 0.5/1. Therefore, the preferred ratio of  $\text{Cl}_2/\text{R-1233zd}$  is considered to be about 1.0/1 to 1.3/1 when only the removal of R-1233zd is desired.

5

#### Example 4

#### Effect of Light Intensity on Photochlorination Performance

A series of experiments were done using the same general procedure as that described in Example 1. However, for each experiment, the light intensity was varied by varying the number of light bulbs used in the Rayonet reactor. Ferrioxalate actinometry was used to measure the radiation received (see The Chemists Companion, A. J. Gordon & R. A. Ford, Wiley Interscience (1972), pages 362-368). All samples were exposed to UV light as described in Example 1 for 1 minute. Then GC analysis was completed as described. The amounts of reagents and experimental results are shown in Table 3 below.

15

Table 3

#### Effect of Light Intensity on Performance in Liquid Phase

Weight G-245fa (g)	Chlorine Flow rate (mL/min)	Chlorine Flow time (sec)	Calculated Moles Chlorine ( $\times 10^5$ )	Calculated $\text{Cl}_2/\text{R-1233zd}$ Molar Ratio	Light Intensity (Einsteins/ $\text{sec} \times 10^3$ )	Conc. of R- 1233zd (%)	Conc. of R-235fa (%)
Feed	—	—	—	—	—	1.04	0.0027
23.1	10.32	118	79.7	1.0	1.317	0.00574	3.02
19.3	10.32	99	66.6	1.0	1.181	0.0764*	0.799*
15.5	10.32	79	55.4	1.0	0.866	0.0112	2.678
14.8	51.1	76	51.1	1.0	0.410	0.1116	2.047

\*Air contamination suspected

This set of experiments shows that, as might be expected for a light-driven reaction, more light results in higher conversions. This effect is evident both in the conversion of R-1233zd to more highly chlorinated species and the conversion of

20

R-245fa to R-235fa. The experimental results can also be used to measure the quantum yield of the process, which is defined as the ratio of the rate of chlorination (in moles/second) and the intensity of light incident on the sample (in einsteins/second). Since an einstein is a mole of photons, this quantity is unitless. We  
5 calculate that the quantum yield measured in this set of experiments is roughly 100.

CLAIMS:

1. A process for removing 1-chloro-3,3,3-trifluoropropene (R-1233zd) or other olefinic impurities from 1,1,1,3,3-pentafluoropropane (R-245fa) comprising
  - (a) contacting a mixture consisting substantially of R-245fa and up to about 20,000 wt. ppm R-1233zd with about 1-5 mols of chlorine for each mol of R-1233zd or other olefins in the presence of ultraviolet light having wavelengths between about 300 and 400 nm providing an exposure greater than zero and at least 0.02 watts-hour/kg of said mixture, thereby reducing the concentration of R-1233zd or other olefins to less than 10 wt. ppm by converting said R-1233zd to 1,2,2-trichloro-3,3,3-trifluoropropane (R-233) or propanes containing greater amounts of chlorine; and
  - (b) separating the R-233 formed in (a) from R-245fa.
2. The process of Claim 1 wherein said R-245fa is chlorinated in part to co-produce 3-chloro-1,1,1,3,3-pentafluoropropane (R-235fa).
3. The process of Claim 1 wherein said ultraviolet light provides an exposure of about 0.02 to 2 watts-hour/kg of said mixture.
4. The process of Claim 1 wherein about 1 to 1.5 mols of chlorine are present for each mol of R-1233zd.
5. The process of Claim 1 wherein the contacting of (a) is carried out at a temperature and a pressure sufficient to assure that R-245fa is liquid.
6. The process of Claim 1 wherein the contacting of (a) is carried out at a temperature and a pressure at which R-245fa is vapor.
7. The process of Claim 1 wherein the temperature is in the range of about -50°C to 200°C.
8. The process of Claim 7 wherein the temperature is in the range of about 25°C to 60°C.

9. The process of Claim 1 wherein the separation of (b) is carried out by distillation.

10. The process of Claim 1 wherein said other olefinic impurities comprise at least one member of the group consisting of R-1223xd, R-1224zb, R-1224xe, and  
5 R-1233xf.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/05656

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C07C17/395 C07C19/08

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 12058 A (ALLIED SIGNAL INC) 24 June 1993 see claims	1
A	US 4 948 479 A (BROOKS WAYNE E ET AL) 14 August 1990 see claims	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

19 June 1997

Date of mailing of the international search report

27.06.97

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Bonnevalle, E

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/05656

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
W0 9312058 A	24-06-93	US 5336377 A	09-08-94
		AU 3243593 A	19-07-93
		BR 9206948 A	28-11-95
		CA 2125775 A	24-06-93
		CN 1074207 A	14-07-93
		EP 0618888 A	12-10-94
		JP 2547519 B	23-10-96
		JP 6510797 T	01-12-94
-----			
US 4948479 A	14-08-90	AT 113023 T	15-11-94
		CA 2014945 A,C	07-12-90
		DE 69013401 D	24-11-94
		EP 0401493 A	12-12-90
		ES 2062154 T	16-12-94
		JP 3024024 A	01-02-91
		JP 7091203 B	04-10-95
		-----	